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**Note**

# Observation of Deformation Process of Polyethylene with an X-Ray TV System

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Since folded chain lamellar crystals were discovered to form spherulites in crystallzable polymers, there have been continuing efforts to gain a better understading of the deformation mechanisms of the polymer solids in terms of structure changes in lamellar crystals. The X-ray studies published so far were carried out on specimens after deformation or during deforming at a low rate sufficient to record X-ray diffraction patterns.[1~6] As polymer solids, amorphous or crystalline, are viscoelastic, the texture relaxed already may furnish little information on the dynamic feature of the polymer microstructure under deformation. Deductions from the static data might lead us to a misunderstanding of the deformation mechanism.

On bulk polyethylene, Tanaka *et al.* observed a stress-induced phase transformation of an orthorhombic unit cell to a monoclinic one.[7] Geil *et al.* studied by means of electron diffraction the effect of draw direction on types of deformation of polyethylene single crystals.[1,8] The latter results could not be directly applied, however, to interpret the deformation behavior of melt-crystallized polymers because of the substantial differences in both microstructure and mode of molecular folding between single crystals and spherulites (bulk polymers).

The purpose of this note is to describe the usefulness of an X-ray television system in studying the deformation mechanism. With this system, the recording speed of the diffraction patterns was so improved that transient features of crystal modification could be observed at a relatively high deformation rate.

## EXPERIMENTAL

Two types of samples were used in the present study. The first sample was a high density polyethylene (Sholex 6009) melt pressed and cooled to room temperature. In this film, the crystallites were confirmed to be randomly oriented under X-ray diffraction examination. In preparing the second sample, the same polymer was melt extruded from a circular die, blowed and cooled to room temperature (EB film). Observations of surface replicas of the film under the electron microscope revealed that the lamellae were oriented normal to the extrusion direction. In addition, the crystallographic *b*-axis was found by X-ray diffraction to be parallel to the film surface and perpendicular to the extrusion

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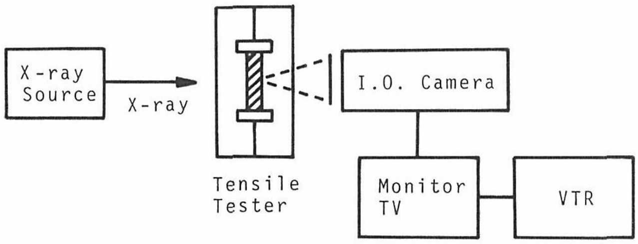



Fig. 1. A block diagram of the X-ray television system and the tensile tester.

direction. Specimens, 20 mm long and 5 mm wide, were cut out of the film at angles 0°, 30° and 90° to the extrusion direction. These are denoted as specimens 0, 30, and 90, respectively.

The test specimens were then deformed in tension along the longer side at a speed of 50 mm/min in a tensile testing machine. Crystallographic data were obtained on a Rigaku-Denki X-ray unit, equipped with a graphite monochromator and a rotating anode which allowed an intense incident beam (CuK$\alpha$) on the specimen. The unit was combined with an X-ray television system, which was composed of an image orthicon camera, a monitor television and a video tape recorder (Fig. 1). An X-ray collimator with a rectangular aperture (0.1 mm $\times$ 0.25 mm) was used to reduce the beam divergence. Since the width of necking region of the deforming specimen was very narrow, about 0.5 mm in our case, the shorter side of the aperture was kept parallel to the draw direction in order to detect the possible structure changes within the necking region as sharply as possible.

## RESULTS AND DISCUSSION

The X-ray photographs from EB film in an undeformed state showed the usual arcs of the orthorhombic modification. When drawn, reflections due to the less common monoclinic form appeared in arcs at the beginning of neck formation in specimen 0 and

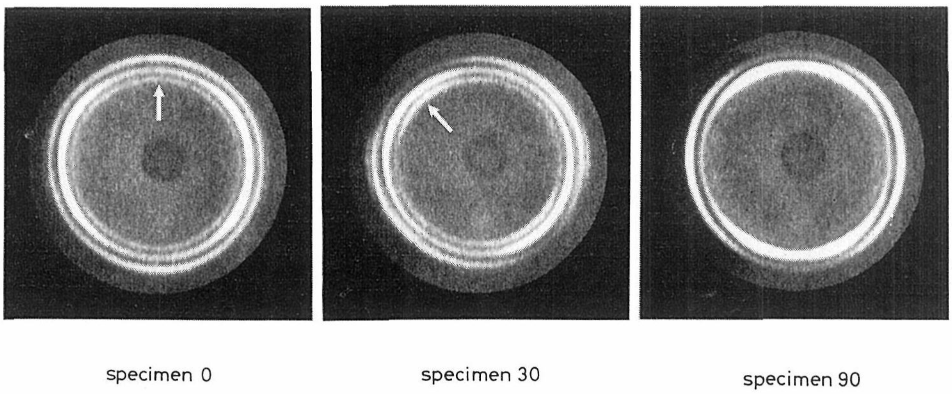



Fig. 2. X-ray diffraction pattern of EB film at the initial stage of neck formation, showing monoclinic reflections from specimen 0 and specimen 30 but no monoclinic reflections (arrows) from specimen 90. Draw direction is vertical.

specimen 30 (Fig. 2). When drawing was stopped, the intensity of the monoclinic reflections decreased rapidly and only the orthorhombic reflections remained, but the monoclinic ones reappear after drawing was restarted. After the neck formation was completed the monoclinic reflections almost disappeared again, and the specimen showed the *c*-axis orientation (fiber structure). On specimen 90 the transformation of the lamellar structure to the fiber structure was accomplished without passing through the monoclinic phase, as judged from the absence of monoclinic reflections.

In conjunction with the results from the electron microscopic observations on the

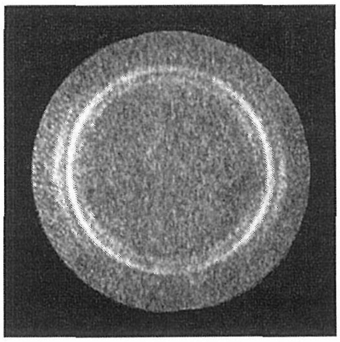
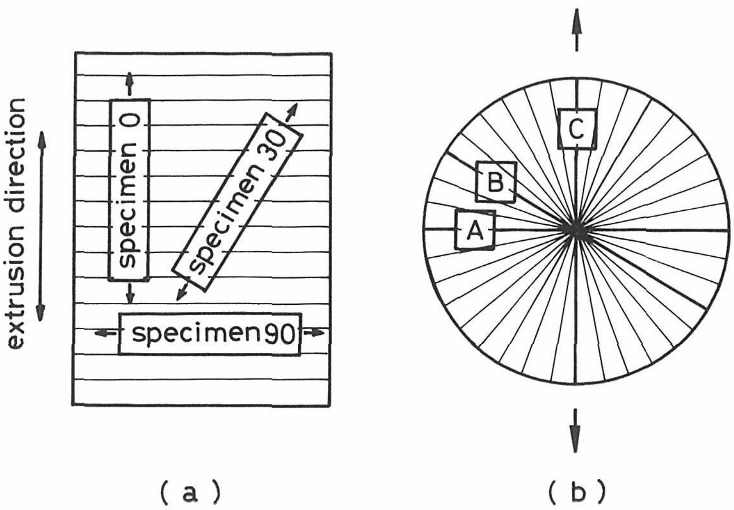


Fig. 3. X-ray diffraction patterns of unoriented polyethylene at the initial stage of neck formation. Draw direction is vertical.




| EB film | (001) mono. intensity | spherulite |
|---|---|---|
| specimen 0 | strong | A |
| specimen 30 | strong | B |
| specimen 90 | very weak | C |

Fig. 4. Relationships between the direction of *b*-axis and that of elongation. Arrows show the direction of elongation, and faint lines indicate that of the *b*-axis. (a) EB film, (b) Spherulite.

lamellar orientation, the transformation of the lamellar structure to the fiber structure appears to take place without passing through the monoclinic phase when the *b*-axes of the lamellae are aligned in the draw direction. Drawing at a fairly large angle (0–60°) to the *b*-axis seems to cause distortion of lamellae and produce the monoclinic form in the initial stage of deformation.

Specimens of unoriented polyethylene, which were aggregates of spherulites, also gave the monoclinic arcs centered on the meridian during deformation (Fig. 3). In polyethylene spherulites, lamellae grow in the *b*-axis direction, that is, the *b*-axis has the radial orientation. When a spherulite is drawn, *i.e.*, stressed uniaxially, the angle between the direction of stress and that of the *b*-axis depends on the position of individual lamella in the sphere. As illustrated in Fig. 4, the angles in the regions A, B, and C are equal to those in specimens 0, 30, and 90, respectively. On the analogy of the deformation behavior of EB film, it is concluded that the monoclinic form appeared at the beginning of neck formation in unoriented polyethylene occurs in the distorted lamellae in regions A and B, whereas the lamellae belonging to region C are turned into fiber structure without passing through the monoclinic phase in the process of the transformation.

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